PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 17/395, 19/08

A1

(11) International Publication Number: WO 97/37955

(43) International Publication Date: 16 October 1997 (16.10.97)

(21) International Application Number: PCT/US97/05656

(22) International Filing Date: 4 April 1997 (04.04.97)

(30) Priority Data:
08/628,064 4 April 1996 (04.04.96) US

(81) Designated States: JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(72) Inventors: YATES, Stephen, Frederic; 1539 S. Kennicott Drive, Arlington Heights, IL 60005 (US). GAITA, Romulus; 6646 Davis Street, Morton Grove, IL 60053 (US).

(74) Agent: CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(54) Title: PURIFICATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (R-245fa)

(57) Abstract

1-Chloro-3,3,3-trifluoropropene (R-1233zd) or other olefin impurities are removed from 1,1,1,3,3-pentafluoropropane (R-245fa) by contacting the R-245fa in the liquid or vapor phase with chlorine in the presence of ultraviolet light providing an exposure of at least about 0.02 watts-hour/kg.

PURIFICATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (R-245fa)

BACKGROUND OF THE INVENTION

This invention relates principally to the purification of 1,1,1,3,3-pentafluoropropane, also designated R-245fa, which has been of particular interest as a replacement for chlorofluorocarbons having similar physical properties, particularly R-113. R-245fa may be prepared by a three-step process involving reaction of chloroform, CCl_4, with vinylidene chloride, $CH_2=CCl_2$, reacting the product with HF to form $CF_3CH_2CF_2Cl$ (R-235fa) and finally, hydrogenation to remove the chlorine atom, as disclosed in pending U.S. Serial No. 08/099,676.

It is characteristic of such reactions that many by-products are formed, containing varying numbers of hydrogen, chlorine, and fluorine atoms on C_1-C_3 compounds. These by-products and the unreacted feed material may be separated by distillation where possible. Some compounds are relatively harmless since their presence does not greatly alter the physical properties for which R-245fa is useful One by-product which must be removed because of its toxicity is 1-chloro-3,3,3,-trifluoropropene (R-1233zd), although only relatively small amounts are typically present in R-245fa as formed. R-1233zd has a boiling point close to that of R-245fa making them difficult to separate by distillation. After distillation of the crude product, R-1233zd will still be present in amounts from about 300 to 20,000 ppm (wt.). It should be reduced to below 20 ppm according to the specifications of the Panel for Advancement of Fluorocarbon Test (PAFTII). Preferably, the R-1233zd should be below about 10 wt. ppm.

Further improvement in methods of purifying R-245fa, particularly with respect to eliminating R-1233zd is desired and the present inventors have discovered a means for purification by photochlorination which will be disclosed in detail below.

In addition to R-1233zd, there may be several other unsaturated by-products present which would be expected to be removed by a process which removes R-1233zd, for example, R-1223xd, R-1224zb, R-1224xe, R-1233xf, and the like

separated from R-245fa. Optionally, R-235fa may be co-produced by chlorination of R-245fa.

Process Conditions

In the process, crude R-245fa containing about 300 to 20,000 wt. ppm of R-1233zd along with minor amounts of other byproducts such as those mentioned above will be contacted with chlorine in the presence of ultraviolet light having a wavelength of about 300 to 400 nm. It should be understood that an ultraviolet lamp may have radiation outside this range also, but that photochlorination requires UV light within this range.

The ultraviolet light will have an intensity which provides an exposure greater than zero and at least about 0.02 watts-hour/kg of the R-245fa mixture. preferably 0.02 to 2.0 watts-hour/kg.

The ultraviolet light may be provided by arc lamps including mercury, argon, or xenon and filament lamps including tungsten and halogen.

Chlorine is introduced into the crude R-245fa stream at a rate sufficient to provide about 1 to 5 mols of chlorine for each mol of R-1233zd, preferably 1 to 1.5.

It has been found that increasing either the ratio of chlorine to R-1233zd (Cl_2/R-1233zd) or the ultraviolet light exposure improves the chlorination of R-1233zd. Generally, we have been able to reduce the R-1233zd to below 10 wt. ppm using a UV exposure above about 0.04 watts-hour/kg but with quite low ratios of Cl_2/R-1233zd. Conversely, much lower UV exposures can be used if higher Cl_2/R-1233zd ratios are used. The Cl_2/R-1233zd ratio and UV exposure may be adjusted to provide the desired set of conditions.

The temperature employed may vary but may be from about -50°C to 200°C, preferably about 25° to 60°C.

The pressure selected will be a convenient value to suit the processing conditions for R-245fa and to assure that R-245fa is a liquid or vapor. as desired

Example 1

Liquid phase purification of R-245fa

The photochlorination of R-245fa was carried out in a 125 mL pyrex pressure vessel equipped with a dip leg inlet and a pressure gauge. This vessel was chilled in ice water and 20.0 grams of impure G-245fa, containing 0.08% R-1233zd was condensed into it. Then, while still cold, a stream of chlorine gas was passed at 10 mL/min through this solution for exactly 52 seconds. We calculate according to the ideal gas law that this should correspond to 3.6×10^{-4} moles of chlorine, or a 1:1 mole ratio with the R-1233zd impurity. The vessel was then allowed to warm to room temperature.

The reactor vessel was placed for 5 minutes at the focus of RPR-100 Rayonet reactor (Southern New England Ultraviolet Company) equipped with 16 RPR-3500 lamps having their peak intensity at a wavelength of 350 nm. Light below 300 nm was removed by the pyrex walls of the pressure vessel. Ferrioxalate actinometry was used to measure the radiation received (see The Chemists Companion, A. J. Gordon & R. A. Ford, Wiley Interscience (1972), pages 362-368) In this vessel under these conditions this procedure gave an incident light intensity of 1.317×10^{-7} einstein/sec (0.0417 watts). (One einstein is an equal to a mol of photons.) A five minute exposure should therefore have supplied 3.95×10^{-5} einsteins of light (0.039 watt-hour/kg).

After exposure, the vapor head of the pressure vessel was sampled by gas chromatography using a 3048 mm long x 3.175 mm diameter column of 1% SP1000 on 60-80 mesh Carbopack B (Supelco Inc.) packing operated at 45°C for 3 minutes and then programmed to increase 8°C/min to 200°C. This stream contained 0.00335 % R-1233zd, and 0.0793 % R-235fa.

Example 2

Vapor phase purification of R-245fa

The photochlorination of R-245fa was carried out in a 125-mL pyrex pressure vessel equipped with an inlet at the bottom and an outlet at the top The reactor vessel was placed at the focus of RPR-100 Rayonet reactor (Southern New

Example 3

Effect of Chlorine Ratio on R-245fa Purity

A series of experiments were done using the same general procedure as that described in Example 1. However, for each experiment, the weight of G-245fa, and the amount of chlorine introduced was changed, so as to explore the effect of changing the ratio of these reactants. All samples were exposed to UV light as described in Example 1 for 1 minute. Then GC analysis was completed as described. The amounts of reagents and experimental results are shown in Table 2 below.

Table 2

Effect of Chlorine Ratio on Performance in Liquid Phase

Weight G-245fa (g)	Chlorine Flow rate (mL/min)	Chlorine Flow time (sec)	Calculated Moles Chlorine (x 10^5)	Calculated Cl_2/R-1233zd Molar Ratio	Conc. of R-1233zd (%)	Conc. of R-235fa (%)
Feed	—	—	—	—	1.04	0.0027
17.3	2.97	30	5.8	0.096	0.935	N.D.
21.5	10.33	30	20.3	0.27	0.54	0.01
9.5	10.32	24	16.2	0.495	0.40	0.191
8.20	10.34	32	21.6	0.76	0.017	1.85
11.8	10.34	60	40.6	1.00*	0.829*	N.D.*
23.7	10.33	160	108.1	1.22	0.0003	0.66
23.9	10.33	180	121.6	1.47	N.D.	4.05

*Air contamination suspected, which will prevent the photochlorination from occurring.

It can be seen that the concentration of R-1233zd decreases as the ratio of Cl_2/R-1233zd is increased. Theoretically one mol of chlorine can react with one mol of R-1233zd to yield one mol of R-233 The results show that at a ratio of about

R-245fa to R-235fa. The experimental results can also be used to measure the quantum yield of the process, which is defined as the ratio of the rate of chlorination (in moles/second) and the intensity of light incident on the sample (in einsteins/second). Since an einstein is a mole of photons, this quantity is unitless We calculate that the quantum yield measured in this set of experiments is roughly 100

9. The process of Claim 1 wherein the separation of (b) is carried out by distillation.

10. The process of Claim 1 wherein said other olefinic impurities comprise at least one member of the group consisting of R-1223xd, R-1224zb, R-1224xe, and R-1233xf.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/05656

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9312058 A	24-06-93	US 5336377 A	09-08-94
		AU 3243593 A	19-07-93
		BR 9206948 A	28-11-95
		CA 2125775 A	24-06-93
		CN 1074207 A	14-07-93
		EP 0618888 A	12-10-94
		JP 2547519 B	23-10-96
		JP 6510797 T	01-12-94
US 4948479 A	14-08-90	AT 113023 T	15-11-94
		CA 2014945 A,C	07-12-90
		DE 69013401 D	24-11-94
		EP 0401493 A	12-12-90
		ES 2062154 T	16-12-94
		JP 3024024 A	01-02-91
		JP 7091203 B	04-10-95